On the Composition of the Waters of the Dee and Don, at Aberdeen, with an Investigation into the Action of Dee Water on Lead Pipes and Cisterns.

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I.—GENERAL CHARACTER OF THE DISTRICTS DRAINED BY THE RIVERS DEE AND DON.

The sources of the Dee are found amidst the lofty granite mountains of Braemar, on the confines of the counties of Banff, Inverness, and Perth. The river flows from thence, in an easterly direction, along a narrow valley, till it falls into the sea at Aberdeen, its length being about 80 miles, or, when measured in a straight line, 65 miles. The river-banks are gravelly, and the alluvial deposits few, and of limited extent. The bounding ridges of the valley are mostly of granite and gneiss. The flow of the water is pretty rapid, the alteration of level between the Linn (16 or 17 miles below the source) and Aberdeen, being nearly 1200 feet. From the small proportion of clay and peat in the valley of the Dee, its waters are usually quite clear; in rainy weather, however, they are often charged with mud from the swollen mountain-torrents. The Dee and its tributaries drain about 900 square miles of country.

The rocks near the sources of the Dee are granite and quartzose mica-slate. Though very insoluble in their nature, these rocks will, by slow decomposition, yield to the water minute portions of silica, potash, and iron. The springs of the Dee must, however, be very pure. Further down, the river receives water that flows over patches of crystalline limestone, and a tributary (the Muick) passes along a *serpentine* range. From these rocks, the water will derive a small proportion of lime and magnesia. Proceeding still farther down, the rocks present no variety; granite and gneiss, with occasional veins of felspar-porphyry, and more rarely, patches of limestone, making up the geology of the district.

The water for the supply of Aberdeen is taken from the Dee about two miles from its mouth, and quite beyond the reach of the tide-water. It percolates through the gravelly sides and bottom into drains, and is thence pumped up to the highest level of the town. It is distributed through iron mains, and taken into houses by small lead pipes, to which lead cisterns, generally of moderate dimensions, are commonly attached. The supply is constant, and amounts to about one million gallons per day.

The district drained by the Don lies immediately north of that drained by the Dee, and is of much less extent. Rising in mossy ground, encircled by granite hills, on the borders of Banffshire, the Don pursues a winding course of about 60 miles to Aberdeen. A straight line from its origin to its termination is about 42 miles. The mountainous region drained by the sources of this river, although mainly granitic, has more limestone and serpentine than exist about the Dee, and hence more lime and magnesia might be expected in the water. At Kildrummy, the Don passes through a range of old red sandstone. A few miles below this the hills recede from the river, and enclose the fine valley of Alford. After emerging from the hilly country at Monymusk, its progress is tortuous and slow, through alluvial meadows and an open country, till within a few miles of its termination, when it again flows rapidly. About 18 miles from the sea it receives its largest tributary, the Ury, which drains a fertile country, and has a course of about 24 miles before losing itself in the Don. After rain, the water of the Ury is commonly tinged yellow with clay, while the Don itself has more of a brown colour from peat. The Don water at Aberdeen is rarely of such limpid clearness as that of the Dee.

II.—COMPOSITION OF DEE WATER.

The specimen (*A*) subjected to analysis by the ordinary methods, was collected some miles up the river, on Sept. 24th, 1850, three days after heavy rain. The river was about its usual size, the rain having been preceded by a long-continued drought. The water had a brownish tint from vegetable matter, and, on close inspection, minute specks and hair-like bodies could be observed floating in it. These could be removed by filtration, which, however, did not sensibly improve the colour. The vegetable matter was perceptible to the taste. The water contained little or no air, and I have observed on several other occasions, that when the water is coloured by organic matter, it is deficient in air. The Dee water, in its ordinary condition is colourless, and is well, often highly, aerated. The solid matter found in a gallon of specimen *A* was constituted as follows:

Lime	0·526	grains.
Magnesia	0·110	„
Potash and soda	0·382	„
Carbonic acid (in combined state) . . .	0·374	„
Sulphuric acid	0·275	„
Chlorine	0·338	„
Silica	0·140	„
Precipitate by ammonia from acid solution .	0·080	„
Organic matter and loss	1·775	„
Total	4·000	

The acids and bases may be arranged thus:

Carbonate of lime	0·850	grains.
Sulphate of lime	0·121	„
„ magnesia	0·323	„
Chlorides of potassium and sodium . .	0·670	„
Phosphate of lime and iron . . .	0·080	„
Silica	0·140	„
Organic matter and loss	1·816	„
	4·000	

In this scheme, I have supposed the sulphuric acid to be increased by ·009 grain, in order to make it take up the whole magnesia. The alkalies were determined together; but in the qualitative examination, potash was readily detected in the residue of 1 gallon.

The dry residue, obtained by evaporating the water, not being deliquescent on exposure, the absence of earthy chlorides was inferred. In the precipitate by ammonia from an acid solution, the presence of lime and iron was detected, but the proof of phosphoric acid was inconclusive. Operating afterwards, however, on the solid contents of a much larger quantity of water (about 15 gallons), this acid was shown pretty distinctly. The dry residue of 1 gallon gave no indication of nitric acid when tried with sulphuric acid and sulphate of iron. Boiled with carbonate of soda, it gave distinct proof of ammonia.

The quantity of organic matter in specimen *A* was much larger than the Dee water usually contains; indeed the brown tint caused by it was very well marked. A portion kept in a glass bottle for some months, deposited a brownish sediment, and became clearer. It was then found to contain only 1 grain of matter volatile on ignition. A specimen (*B*) taken from the same part of the river on the 15th of February, 1851—the river being of its usual size, and the water clear and colourless—gave 3 grains per gallon of solid matter, of which only $\frac{4}{10}$ths of a grain were volatilized by ignition. It is in accordance with general experience that organic matter in water is least abundant during the winter season. A gallon (*C*) drawn from the laboratory pipe on the 26th of September (the water being colourless), left the same quantity of dry residue, and gave off about 0·8 grain on ignition. In experiments at different times, I have thus found the solid matter (dried at 212°) to vary from 3 to 4 grains per gallon; and the matter volatilized by a low red heat (generally reckoned organic matter, though it probably always exceeds the true organic matter in amount) to range from $\frac{4}{10}$ths to $1\frac{3}{4}$ grains.

III.—ACTION OF CLARK'S SOAP TEST ON DEE WATER.

In many trials of Dee water, taken either directly from the river, or from the laboratory pipe, the hardness was found to vary between 1°·1 or 1°·2, and 1°·75. But different trials of the same specimens have sometimes varied a little—such a variation as I have been accustomed to find in solutions of very low degrees of hardness, especially when this hardness is caused partly by magnesia. In specimen *A*, the hardness varied in three trials from 1°·1 to 1°·14. After standing a day or two, the lathers could not be renewed without a further addition of soap-test, raising the hardness thus in two of the cases to 1°·36. Taking the mean between the highest and lowest, we may assume the hardness of specimen *A* to be 1°·23; and this agrees accurately with three trials made on water drawn from the laboratory pipe on the 28th of September, which should not have differed much from river water of the 24th. The greatest hardness observed was in specimen *B*, taken direct from the river on the 15th of February. It turned out 1°·75; but as the specimen was highly aerated, it is just possible that a little of this apparent hardness may have arisen from carbonic acid.

In specimen *A*, I distinguished the hardness caused by lime from that caused by magnesia, by means of the soap-test, as follows: A mixture of equal bulks of standard lime solution 20° and distilled water was tried, and the hardness noted. A similar mixture of same solution 20° and specimen *A* was then made, and the hardness determined. The difference was 0°·47. This, multiplied by 2 (as the Dee water operated on was only half the standard quantity), gives 0°·94, the hardness caused by lime; and subtracting this from 1°·23, the total hardness, leaves 0°·29 as the hardness resulting from magnesia. By an extended course of experiments, I had previously satisfied myself that the soap-test is not affected by any quantity of magnesia under 6° or 8°, if associated with at least 10° of lime; hence the contrivance of the above experiments. If the whole lime in the water, as given in the preceding analysis, page 325 (omitting what may exist in the precipitate by ammonia), be calculated as carbonate, the amount will correspond exactly to that indicated by the soap-test, namely, 0·94 grain; and if the magnesia, in like manner, be calculated as carbonate of lime, it will turn out 0·26 grain, differing very little from the soap-test result; and in the case of magnesia, it is to be expected that the ordinary analysis will give under the truth. The quantity of pyrophosphate of magnesia, afforded by a gallon of water (*A*), I have noted at 0·30 grain. If this be made 0·32, it will correspond exactly with the indication of the soap-test. This new application of the soap-test promises to be of considerable utility.*

IV.—COMPOSITION OF DON WATER.

Two specimens were examined. One (*A*) was taken on the 4th of October, from the river about a mile from its embouchure, quite beyond the reach of the tide. The other (*B*) was collected near the Bridge of Alford (about 35 miles up, counting the windings of the river), on the same day, and about nine hours previous to the collection of specimen *A*. The river was in its average condition. Specimen *A* was tinged brown with vegetable matter, which also affected the taste. Flocculi of organic matter were seen in it, and brown specks of iron and organic matter, speedily subsiding on rest. No air-bubbles emitted on exposure. By careful evaporation, the solid matter was found to be in the proportion of 8·64 grains per gallon, and of this there were 3·04 grains volatilized by ignition. The composition of the dry matter was as follows:

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* The Culter Burn, a large tributary of the Dee, which drains the Loch of Skene and surrounding country, I found to contain at its confluence with the Dee (about 8 miles up), on the 26th of September, 6 grains of fixed salts per gallon, with 2 or 3 grains of organic matter additional. Hardness 3°·1.

Lime	1·29	grains.
Magnesia	·34	„
Alkaline chlorides, containing 0·74 of chlorine	1·32	„
Carbonic acid (in combined state)	·96	„
Sulphuric acid	·76	„
Silica	·60	„
Precipitate by ammonia from acid solution	·38	„
Organic matter	3·00	„
Total	8·65	

The acids and bases may be taken thus:

Carbonate of lime	2·18	grains.
Sulphate of lime	·17	„
„ magnesia	1·00	„
Chlorides of potassium and sodium	1.32	„
Phosphate of lime and iron	·38	„
Silica	·60	„
Organic matter	3·00	„
Total	8·65	

Specimen *B* was very faintly tinged with vegetable matter, and contained some floating specks of the same. On evaporation, it left at the rate of 5 grains solid matter per gallon, of which 3·8 were fixed salts, and 1·2 volatile (organic matter).

Hardness of Don Water.—The soap-test with specimen *A* gave 3½°, with *B*, 2½°. The hardness of *A*, calculated from the above table, is, for lime, 2°·32, for magnesia, 0°·82; together equal to 3°·14. The phosphates would add something to this. I had not an opportunity of applying the new soap-test process to this specimen in its original state. After being kept four months in a stoneware jar, the water was found to have increased in hardness to 4°·2. The total solid matter per gallon had increased to 9·6 grains, while the organic matter remained precisely as at first, 3·04 grains. On applying the soap-test to separate lime or magnesia, in the manner already described, the hardness, owing to lime, was found to be 3°·4, and that from magnesia 0°·8: while the lime had thus been increased by impurity from the jar, the magnesia appears to have remained unaltered.

IV.—ACTION OF DEE WATER ON LEAD.

Under this head I have recorded about forty trials, made at different times, and on water from houses in various parts of the town; besides upwards of a dozen experiments with lead bars in specimens of water not previously in contact with lead. In the sequel, I shall make such a selection from these trials as may serve to bring out the conclusions arrived at.

Mode of operating.—The test used was sulphuretted hydrogen; the water being previously acidulated with hydrochloric acid, and the gas transmitted a sufficient length of time. In the earlier trials I used only one or two pints of each specimen, but it soon became apparent that much greater delicacy was attainable by employing a larger quantity. In proceeding with the experiments, therefore, I operated uniformly on a gallon, contained in a glass beaker, of such dimensions that the water had a depth of 10½ inches. By placing the beaker on a piece of white paper, and looking downwards, I was able to appreciate a very slight change in tint. Another similar vessel, with the same quantity of water, was always placed by the side of the first, for the sake of comparison. In estimating the quantity of lead present in any case, I had recourse to a very simple expedient. A solution of lead was prepared of definite strength; chloride of lead was used at first, but afterwards pure nitrate, as more convenient. 1·6 grain of nitrate was dissolved in 1000 grains of distilled water, so that the solution contained 1 of metallic lead in 1000. From an accurately graduated measure, I dropped this solution into a gallon of water containing no lead, until, on transmission of sulphuretted hydrogen, the same depth of tint was developed as in the particular case on trial. Having come as near as possible to the right quantity in this way, I commonly then made a new mixture, adding at once the ascertained quantity of lead to a gallon of water, and transmitting the gas. If the two trials corresponded, the experiment was finished, but in case of any discrepancy, the trial was repeated. This method, I believe, will give very accurate results, until the quantity of lead exceeds ¼ grain per gallon, when the colour gets so dark that slight differences cannot well be discriminated. I found that $\frac{1}{100}$th of a grain of lead, added to a gallon of pure clear water, gave a tint quite perceptible, that is, 1 of metallic lead in 7 millions; and a less quantity could readily be distinguished by careful comparison. Even in specimens previously containing a considerable proportion of lead, the difference of $\frac{1}{100}$ of a grain was plainly visible. Here is an instance: A gallon of Dee water, taken from a leaden pipe, having given a certain tint with sulphuretted hydrogen, a gallon of Dee water, not containing lead, was placed beside it, and 80 grains of the standard solution (containing 0·08 grain of lead) well mixed. By the action of sulphuretted hydrogen, the tint produced was a little lighter than in the other; 10 drops more made the tints equal; and again 10 drops rendered the last somewhat darker than the first. Now every 10 drops of solution contained $\frac{1}{100}$ of a grain of metallic lead.

The preliminary acidulation with hydrochloric acid is very essential when the water under trial happens to contain any iron. In some spring waters that I examined, there was a blackening caused by sulphuretted hydrogen, from the presence of iron in combination with organic matter. Acidulation with hydrochloric acid entirely prevents this blackening, or destroys it after it has been produced, leaving a milkiness in the water, from deposition of sulphur. To ascertain if the hydrosulphuric acid test would be affected by a minute quantity of iron, I dissolved 1 grain of the pharmaceutical ammonio-tartrate (which would contain about $\frac{1}{7}$th of a grain of metallic iron, or $\frac{1}{5}$th grain of red oxide) in a gallon of water. The solution had a greenish-yellow tint. On transmitting the gas, there was no change for some time, but ultimately an evident darkening, with deposition of sulphur.

Selection of trials of Water from House-pipes (*lead*). — Specimens taken during the day, when the water would be in its usual condition, unless stated otherwise.

1. Pipe about 16 yards long—no cistern—no indication of lead.
2. Pipe 12 or 15 yards—no cistern—specimen drawn first in the morning showed a trace of lead (less than $\frac{1}{100}$ of gr. per gallon), specimen drawn at mid-day—no lead.
3. Pipe about 36 yards—no cistern—about $\frac{1}{30}$ of gr. metallic lead per gallon. On another occasion, this pipe gave rather more lead.
4. Pipe upwards of 100 yards—no cistern—tried on different days, the quantity of lead varied from $\frac{1}{30}$ to $\frac{1}{40}$ gr. per gallon.
5. Pipe 16 or 18 yards—small cistern—lead under $\frac{1}{100}$ gr. per gallon.
6. Pipe about 24 yards—cistern—several families supplied, and much water used—no indication of lead.

7. Pipe about 15 yards—cistern— $\frac{1}{50}$ gr. of lead per gallon.

8. Pipe about 30 yards—cistern—about $\frac{1}{35}$ gr. of lead per gallon.

9. Pipe about 100 yards, leading into cistern with about two cubic feet of water,—$\frac{1}{20}$ gr. of lead per gallon. This being the largest quantity I have found in any water in ordinary domestic use, I made particular inquiries in regard to the health of the family. Nothing unusual had ever been noticed, except that, on coming into town for the winter (the family lived in the country during summer), the children speedily lost colour. This, of course, is usually attributed to the *air* of the town, but it would be worth inquiring how much of the effect in such cases is due to the *water*. This case, however, shows that water containing $\frac{1}{20}$th of a grain of metallic lead per gallon (equal to $\frac{1}{15}$ gr. carbonate), may be used habitually without any notable injurious results. Mr. W. Herapath related a case in the "Times" (14th Sept. 1850), where $\frac{1}{9}$th of a grain of lead per gallon deranged the health of a whole community. The limit of the deleterious action would seem thus to be somewhere between $\frac{1}{10}$th and $\frac{1}{20}$th of a grain.

10. The leaden pipe supplying Marischal College afforded some instructive points. It is upwards of 100 yards long. Specimens of water, drawn before entering any of the cisterns, contained, as stated in case 4, from $\frac{1}{30}$ to $\frac{1}{40}$ of a grain per gallon. About the middle of the pipe, a branch is taken off to the porter's house, where it discharges into a small cistern. Water taken from this at different times contained $\frac{1}{25}$ to $\frac{1}{30}$ of a grain of lead per gallon. The college pipe near its termination supplies a cistern containing usually about 10 cubic feet of water. A specimen taken direct from this cistern I found to contain $\frac{1}{12}$ or $\frac{1}{13}$ of a grain of lead. A specimen taken at the same time from a pipe that proceeds from this cistern about 20 yards, contained $\frac{1}{11}$ of a grain. The pipe was allowed to run a good deal before the specimen was drawn. Tried at various times, this pipe afforded from $\frac{1}{8}$ to $\frac{1}{14}$ of a grain of lead per gallon. Another pipe from the same cistern, after remaining a day or two unused, contained sometimes $\frac{1}{5}$, or even $\frac{1}{4}$ of a grain per gallon.

Selection from Experiments with Lead Bars.—1. Bar of bright lead, immersed (to the extent of 23 square inches of surface) in 2 pints of Dee water—left 48 hours—water remained clear—no deposit—a thin whitish film had formed on lead. The water, after filtration through double filter, contained about $\frac{1}{100}$ of a grain of lead per gallon.

2. Parallel experiment with distilled water: water speedily became

milky—abundant white deposit. Passed several times through double filter, but milkiness not removed. After standing two days, the white matter subsided, and the water then filtered clear. No lead whatever in solution. (The oxide was probably entirely converted into insoluble carbonate by exposure.)

3. Bar No. 1 immersed, without cleaning, in 2 pints of Dee water, and left 48 hours—no deposit. Passed through double filters, the water contained about $\frac{1}{20}$ of a grain of lead per gallon.

4. Bright bar, in 3 pints of Dee water—32 square inches immersed—left 24 hours—filtered—contained trace of lead.

5. Same bar, without cleaning, in 2 pints—26 inches immersed—left 48 hours—filtered—contained $\frac{1}{20}$ of a grain of lead per gallon.

6. Lead bar tarnished in air, immersed (to 30 square inches) in 3 pints—left 48 hours—filtered—$\frac{1}{20}$ of a grain of lead per gallon.

7. The bars used in experiments 5 and 6, were placed, without cleaning, in similar quantities of water, and left 48 hours—not filtered. The water from bar 6 contained about $\frac{1}{10}$ of a grain of lead per gallon. The water from bar 5 contained more.

8. The bar from experiments 5 and 7 being again immersed without cleaning, and left 48 hours, the water unfiltered contained much more lead than in last experiment—about $\frac{1}{6}$ of a grain per gallon.

9. Same bar, left 48 hours, in 2 pints—water passed through double filter, contained about $\frac{1}{10}$ of a grain (or rather more) of lead per gallon.

10. Bar of bright lead, immersed in 2 pints of Dee water for 4 days. The water had been kept for some time in a jar, in a warm room, so that a great part of the air had escaped from it. After filtration the water contained a mere trace of lead. Bar immersed again, without cleaning, in other 2 pints of same water, and left for 2 days. Water (filtered) contained more lead than in last case, but still not much.*

From these experiments, it appears that Dee water acts more readily upon tarnished or crusted lead, than upon the bright metal; that the lead taken up by the water is separated to a small extent by paper filters; and that when a crusted bar is immersed for a certain time in water, dried, and immersed again for the same time, the action is greater the second time than the first; dried and immersed a third time, the action is still greater. (So that a lead cistern, alternately filled and emptied, is more unsafe than one kept constantly at the same level, both being freely exposed to the air.)

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* The lead used in these experiments was the kind commonly employed for lining cisterns—7 or 8 lbs. to the square foot. Fresh portions of Dee water, not previously contaminated by lead, were used in each case.

From the foregoing observations I conclude that the action of Dee water on lead is comparatively feeble, but yet that by prolonged contact, more especially when there is free exposure to air, as in cisterns, a dangerous quantity of that metal may be taken up. With lead pipes of moderate length, and no cisterns, no danger whatever is to be apprehended. With small cisterns, and a pretty constant use of the water, there is also no danger; but the risk increases with the length of the pipe, the size of the cistern, and the time the water lies unused. When large cisterns are required for general domestic use, I think it would be prudent to have them lined with gutta percha or some other innocuous material. With an uninterrupted supply, such as is enjoyed in Aberdeen, and with an improved form of tap, cisterns might probably to a great extent be dispensed with.

In some cases it has appeared to me that old pipes are more acted upon than new; the differences, however, may have arisen from impurities in the lead, or from other special causes not detected. I am also inclined to think that the action on lead depends greatly on the aeration of the water. In rainy weather, when the Dee water is coloured and contains little air, the quantity of lead dissolved in any case appears to be less than when the water is clear and well aerated. This observation has been confirmed to some extent by the experiments with lead bars, but I am not prepared to state it unreservedly as a rule.

Note explanatory of the Degrees of Hardness mentioned in the preceding Paper.

By *Hardness* in a water is meant the property of destroying soap. This property in natural waters is due mainly to compounds of lime and magnesia; carbonate of lime, or chalk, being one of the most frequent causes of hardness.

By a *degree of hardness* is meant as much hardness as would be produced by the presence of 1 grain of chalk per gallon. Thus, at page 6, the hardness of Don water is said to be 3½°, meaning thereby that it destroys as much soap as a solution of chalk in pure water at the rate of 3½ grains in a gallon.